Oxygen Containing Compounds - III

Carboxylic Acids & Derivatives

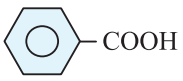
CARBOXYLIC ACIDS [–COOH] Section - 1

The organic compounds which contain the carboxylic acid functional group, $-\overset{\overset{O}{\|}}{C}-OH$ are called as Carboxylic acids. The carboxylic acids ionise in water to give H^+ ions and hence they are acidic in nature.

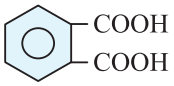
Important Aliphatic acids

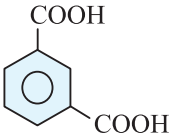
$HCOOH$	Formic acid	CH_3COOH	Acetic Acid
$(CH_3)_2CHCOOH$	Isobutyric acid	$CH_2=CHCOOH$	Acrylic acid
$CH_3CH=CHCOOH$	Crotonic acid (*cis* and *trans*)	$CH_3COCOOH$	Pyruvic acid (α-keto acid)

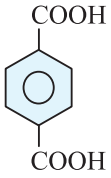
Important Aromatic acids


Benzoic acid

$CH_3-C_6H_4-COOH$ (o, p, m Toluic acid)


Phthalic acid


Isophthalic acid

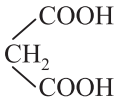

Terphthalic acid

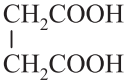

Salicylic acid

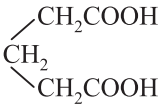

Anthranilic acid
(2-Aminobenzoic acid)

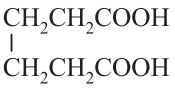
Important Dicarboxylic acids

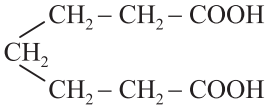

Oxalic acid

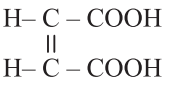

Malonic acid

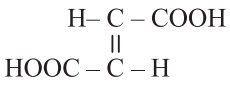

Succinic acid


Glutaric acid


Adipic acid


Pimelic acid


Cis-Maleic acid


Trans-Fumaric acid

Preparation :

1. From Grignard Reagent : $RMgBr + O=C=O \longrightarrow R-\overset{\overset{O}{||}}{C}-O-MgBr \xrightarrow{H_3O^+} RCOOH$

(Dry ice)

2. From Alkenes :

(a) $RCH=CH_2 \xrightarrow{(O)} RCOOH + CO_2 + H_2O$

$RCH=CHR' \xrightarrow{(O)} RCOOH + R'COOH$

(b) Carboxylation : $CH_2=CH_2 + CO + H_2O \xrightarrow[400^\circ C]{H_3PO_4} CH_3CH_2COOH$

$RCH=CH_2 + CO + H_2O \xrightarrow[400^\circ C]{H_3PO_4} R-\underset{\underset{CH_3}{|}}{CH}-COOH$

3. Use of Alkoxide ion

$RO^-Na^+ + CO \xrightarrow[\text{under pressure}]{\Delta} RCOONa \xrightarrow{H^+} RCOOH$

$CH_3O^-Na^+ + CO \xrightarrow[\text{Under pressure}]{\Delta} CH_3COONa \xrightarrow{H^+} CH_3COOH$

4. Oxidation :

(a) Of Alcohols : $RCH_2OH \xrightarrow{(O)} RCOOH$

- Strong Oxidising agents : $K_2Cr_2O_7/H^+$ or $KMnO_4/H^+$
- Mild Oxidising agents : MnO, CuO (Fehling's solution), Ag_2O (Tollen's Reagent), $FeSO_4 + H_2O_2$ (Fenton's reagent) and PCC with Ag_2O. These are used for preparing unsaturated acids as none of these oxidise double bonds.

$RCH=CHCH_2OH \xrightarrow{PCC} RCH=CHCHO \xrightarrow{Ag_2O} RCH=CHCOOH$

(direct conversion of $RCH=CHCH_2OH$ to $RCH=CHCOOH$ with H_2CrO_4)

(b) Of Aldehydes and Ketones :

$RCHO \xrightarrow{(O)} RCOOH$

$RCOCH_2R' \xrightarrow{(O)} RCOOH + R'COOH$

(Ketones are oxidised by strong oxidising agents such as hot $K_2Cr_2O_7/H^+$ or conc. HNO_3 to give mixture of acids)

$Ar-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[2.\,H_3O^+]{1.\,X_2/NaOH} ArCOOH + CHX_3\downarrow$ (Haloform reaction)

- Methyl ketones are oxidised by $NaOH/I_2$ (Iodoform Test) to give (Ar : aryl or R) sodium salt of carboxylic acids.

(c) Of Alkyl benzene : $C_6H_5-R \xrightarrow{(O)} C_6H_5COOH$

Note : R should not be tertiary (3°) alkyl group.

$C_6H_5-CH=CHR' \xrightarrow{(O)} C_6H_5COOH + R'COOH$

Alkenyl benzene

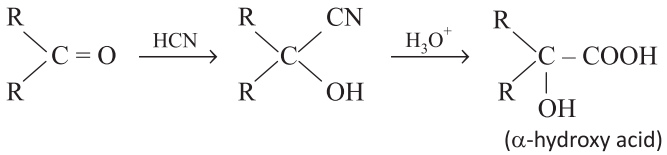
5. Hydrolysis :

(a) Of Nitriles : $RX \xrightarrow{KCN} RCN \xrightarrow[H^+]{H_2O} R-COOH + NH_4^+$ [Step up process]

➤ Hydrolysis of cyanides with OH^-/H_2O first leads to the formation of amides and then they are subsequently hydrolysed to acids.

$$RCN \xrightarrow{^-OH/H_2O} RCONH_2 \xrightarrow{H_3O^+} RCOOH$$

(b) Of Cyanohydrins :



(α-hydroxy acid)

(c) Of Trihalides : $R-C-Cl_3 \xrightarrow{\text{aq. KOH}} R-C-(OH)_3 \xrightarrow[-2H_2O]{\text{aq. KOH}} RCO\bar{O}\overset{+}{K} \xrightarrow{H_3O^+} RCOOH$

(d) Of Esters, Amides, Acid halides and Anhydrides (Acid derivatives) :

$$RCOOR' \xrightarrow[\text{or aq. NaOH}]{H_3O^+} RCOOH + R'OH$$

$$RCONH_2 \xrightarrow[\Delta]{H_3O^+} RCOOH + NH_4^+$$

$$RCOCl \xrightarrow{H_3O^+} RCOOH$$

$$(RCO)_2O \xrightarrow{H_3O^+} 2\,RCOOH$$

Amides when boiled with Nitrous acid (HONO) are converted to acids along with evolution of N_2 gas.

$$RCONH_2 + HONO \longrightarrow RCOOH + N_2 + H_2O$$

6. Malonic Ester Synthesis of monocarboxylic acids :

➤ $\underset{\text{Diethyl malonate}}{CH_2(COOC_2H_5)_2} \xrightarrow{H_3O^+} CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$

➤ $\underset{\text{Diethylmalonate}}{CH_2(COOC_2H_5)_2} \xrightarrow{C_2H_5ONa} \underset{\text{Sodium Diethylmalonate}}{\overset{+}{Na}\bar{C}H(COOC_2H_5)_2}$

(Malonate has an active methylene group, which loses αH-atom to form the carbanion)

$$RX + \underset{\text{Sodium diethylmalonate}}{\overset{+}{Na}\bar{C}H(COOC_2H_5)_2} \xrightarrow[-NaX]{S_N2} R-CH(COOC_2H_5)_2 \xrightarrow{H_3O^+} \underset{\text{Alkyl malonic acid}}{R-CH(COOH)_2}$$

$$R-CH(COOH)_2 \xrightarrow[-CO_2]{\text{Heat}} RCH_2COOH$$

7. Arndt-Eistert Reaction :

$$R-COCl \xrightarrow[\substack{2.\ Ag_2O \\ 3.\ H_2O}]{1.\ CH_2N_2} RCH_2COOH$$

(Observe that acid formed has one extra carbon than parent acid halide).

8. Preparation of Formic acid :

(a) Formic acid is obtained by heating carbon mono-oxide with an alkali. The acid is regenerated by action of H_2SO_4.

$$CO + NaOH \xrightarrow{473\,K,\ 10\ atm} HCOONa \xrightarrow{H^+} HCOOH$$

(At room temperature CO does not react with NaOH)

(b) $\begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\text{glycerol, 383 K}} HCOOH + CO_2$

9. Preparation of Acetic acid :

CH_3COOH is a by-product of alcohol industry.

$$\text{Sugar and starches} \xrightarrow{\text{fermentation}} CH_3CH_2OH \xrightarrow[\text{acetobactor}]{\text{enzyme, } O_2} \underset{\text{(vinegar)}}{CH_3COOH}$$

$$CH_3OH + CO \xrightarrow[\text{heat, pressure}]{\text{Rh catalyst}} CH_3COOH$$

$$CH \equiv CH \xrightarrow{H_2O,\ HgSO_4,\ H_2SO_4} CH_3CHO \xrightarrow[\text{cobalt acetate 353 K}]{O_2} CH_3COOH$$

10. Preparation of Aromatic acid :

Aromatic acids are prepared by oxidation of alkyl benzenes. The better method for the preparation of aromatic acids is by the hydrolysis of aryl cyanides.

$$C_6H_5NH_2 \xrightarrow[0-5^\circ C]{NaNO_2/HCl} C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5CN \xrightarrow{H_3O^+} C_6H_5COOH$$

Note : $ph - CH_3 \xrightarrow[\Delta]{KMnO_4 - KOH} ph - COOK \xrightarrow{H_3O^+} ph - COOH$

Aromatic acids are also prepared using aromatic Grignard Reagent. To illustrate refer to the following plan.

➤